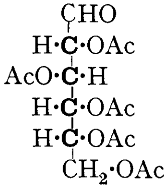
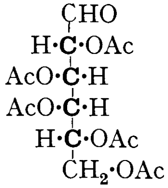
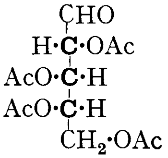
155. *The Rotatory Dispersion of Organic Compounds. Part XXV. Open-chain Derivatives of Arabinose, Fructose, and Fucose. Optical Cancellation in Penta-acetyl μ-Fructose.*

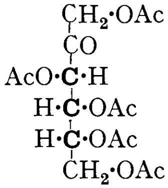
By W. C. G. Baldwin, M. L. Wolfrom, and T. M. Lowry.

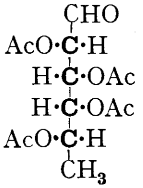
In Part XXIII (J., 1933, 1179) it was shown that, although the asymmetric carbon atoms of penta-acetyl μ-glucose and penta-acetyl μ-galactose, (I) and (II), contribute a *positive* high-frequency term to the rotatory power of these compounds, the corresponding term in tetra-acetyl μ-arabinose (III) vanishes. The whole of the rotatory power of this compound therefore appears to be due to the " induced dissymmetry " of the aldehydic group. In the present paper, the same phenomenon is shown to occur in penta-acetyl μ-fructose (IV) (Wolfrom and Thompson, *J. Amer. Chem. Soc.*, 1934, **56**, 880), a compound in which the three asymmetric carbon atoms are enantiomorphously related to those of the arabinose acetate, but are linked to the radical $CH_2 \cdot O \cdot CO \cdot CH_3$ instead of to a hydrogen atom. Data are also given for tetra-acetyl μ-fucose (V) (Wolfrom and Orsino, *ibid.*, p. 985), which behaves in much the same way as penta-acetyl μ-galactose (II), the four asymmetric carbon atoms of which are enantiomorphously related to its own, but are linked (at the opposite end from the aldehydic group) to methyl instead of to the radical $CH_2 \cdot O \cdot CO \cdot CH_3$. A number of open-chain derivatives of arabinose and fructose were also examined. These could only be studied in the region of transparency, in which the rotatory dispersion appeared to be simple; but definite evidence was obtained that the process of optical cancellation does not extend to this series of derivatives.


(I.) Penta-acetyl μ-*d*-glucose.


(II.) Penta-acetyl μ-*d*-galactose.


(III.) Tetra-acetyl μ-*l*-arabinose.


(IV.) Penta-acetyl μ-*d*-fructose.


(V.) Tetra-acetyl μ-*l*-fucose.

Arabinose and Fructose.—Optical cancellation implies that, when allowance has been made for the low-frequency partial rotations of an optically active absorption band, the residual high-frequency rotations are negligible. Thus, in the case of tetra-acetyl μ-arabinose, the difference curve (obtained by subtracting the calculated partial rotations of the aldehydic group from the observed total rotations of the acetate) cuts the axis of wave-lengths in four points; and the areas of the loops on either side of the axis are so nearly equal that no definite positive or negative sign can be attributed to the residual high-frequency rotation. The cancellation of the partial rotations of the asymmetric carbon atoms in this compound is, however, accompanied by an equality in magnitude of the negative and positive maxima which is more precise than the theoretical dispersion equations would lead us to expect. In particular, Kuhn and Braun's formula forecasts a difference of 200° between the magnitudes of the positive and the negative maximum associated with the aldehydic absorption band, whilst Lowry and Hudson's formula forecasts a difference of 30°. The latter difference is, however, of the same order of magnitude as the unsmoothed ripples on the curve of residual rotations. It is therefore at present impossible to say whether the two maxima, on the curve which represents the isolated partial rotations of the aldehydic radical, (i) should be exactly equal in magnitude, as experiment appears to indicate, or (ii) should differ by about 2%, as the second dispersion formula suggests. Since, however, this formula is admitted to be only a further approximation towards the ideal, we prefer to regard the equality of the negative and the positive maximum as a valid rough-and-ready test of optical concellation, and to ignore the small inequalities predicted by our present imperfect formula.

TABLE I.

Maximum Specific Rotations of Open-chain Acetates.

	First maximum.	Reversal.	Second maximum.
I.	− 464° at 3113 Å.U.	2969 Å.U.	+ 755° at 2600 Å.U.
II.	−1090 ,, 3113 ,,	2925 ,,	+1420 ,, 2650 ,,
III.	−1145 ,, 3122 ,,	2909 ,,	+1145 ,, 2678 ,,
IV.	500 ,, 3020 ,,	2830 ,,	− 500 ,, 2580 ,,
V.	1130 ,, 3150 ,,	2980 ,,	−1755 ,, 2702 ,,

The maxima for the four aldehydes and one ketone which have now been examined are set out in Table I. In accordance with the conclusion reached above, the *equality* of the two maxima, ± 500°, in the rotatory-dispersion curve of penta-acetyl μ-fructose, is once more within the limits of experimental error. The *signs* of the maxima are, however, reversed in the two compounds, since the asymmetric carbon atoms, which are responsible for the induced activity of the aldehydic group, are themselves opposite in sign. As a further point of contrast, the *range* between the two maxima is reduced from 2290° in the aldehyde to 1000° in the ketone, in which the carbonyl group evidently develops a much smaller induced activity. The change from the aldehyde to the ketone is also accompanied by a displacement of the *wave-length* of the maximum of selective absorption from 2900 to 2830 Å.U., of the maximum of circular dichroism from 2910 to 2806 Å.U., and of the reversal of sign from 2909 to 2830 Å.U. These differences correspond with the change of wave-lengths from $\lambda_0 = 2850$ to 2700 Å.U., which is observed on passing from aldehyde to acetone.

Galactose and Fucose.—An interesting comparison between the aldehydic acetates of galactose and fucose can be made with the help of Table II, in which the partial molecular rotations of the asymmetric carbon atoms and of the aldehydic or ketonic group are set out separately for the yellow sodium line.

TABLE II.

Partial Molecular Rotations, $[M]_D$, *of Aldehydic Sugars.*

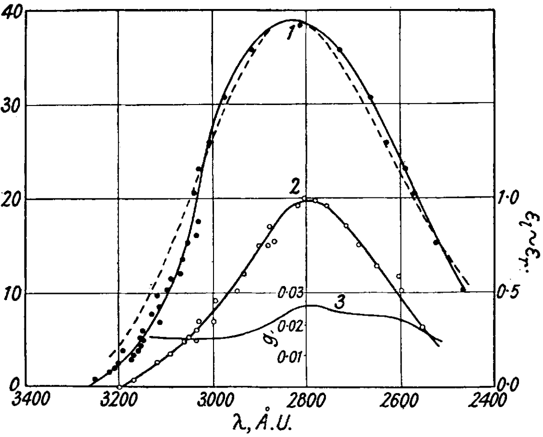
		I.	II.	III.	IV.	V.
Partial rotation of CO group	=	$-109°$	$-238°$	$-188°$	$+119°$	$+239{\cdot}0°$
Partial rotation of other groups	=	$+89$	$+145$	$[-9]$ *	$[+15]$ *	$-105{\cdot}5$
Total rotation	=	-20	-93	-197	$+134$	$+133{\cdot}5$

* The residual rotations $-9°$ and $+15°$ may be attributed to the failure of the theoretical formula to give equal maxima of opposite sign, and should not be regarded as real.

Galactose and fucose have the same configurations as arabinose and fructose as regards the first three asymmetric carbon atoms; but they contain also a *fourth* asymmetric carbon atom, in which the radicals are on the same side as in the first atom. This additional asymmetric carbon atom gives rise directly to a large high-frequency partial rotation, $[M]_D + 145°$, in the galactose acetate, where the fourth asymmetric group is $CH(OAc){\cdot}CH_2{\cdot}OAc$, and $[M]_D - 105°$ in fucose, where it is $CH(OAc){\cdot}CH_3$; but this fourth atom is so remote from the aldehydic group that the inactive terminal group ($\cdot CH_2{\cdot}OAc$ or CH_3), although it has a substantial influence on the rotatory power of the asymmetric carbon atom to which it is attached, does not appear to have any effect at all on the aldehydic group. In these circumstances, the induced activity of this group reaches almost identical maximum values of $-238°$ in the galactose acetate (II) and $+239°$ in the fucose acetate (V), the induced activity being, as usual, opposite in sign to the fixed activity of the asymmetric carbon atoms.

FIG. 1.

Absorption and Circular Dichroism of Penta-acetyl μ-Fructose.



Curve 1. *Molecular extinction coefficients, ε, in chloroform observed (full line) and calculated from Hudson's general equation with n = 2 (broken line).*

,, 2. *Circular dichroism,* $\epsilon_l \sim \epsilon_r$.

,, 3. *Dissymmetry factor,* $(\epsilon_l \sim \epsilon_r)/\epsilon$.

The elimination of the *fourth* asymmetric carbon atom of galactose or fucose reduces the induced activity of the aldehydic group to $[M]_D - 188°$ in the arabinose acetate (III); and the reversal of sign of the *third* asymmetric carbon atom reduces it to $[M]_D - 109°$ in the glucose acetate (I). A similar reduction to $[M]_D + 119°$ occurs when the aldehydic radical of the arabinose acetate is converted into a ketonic radical in the fructose acetate (IV) of opposite sign.

Form of the Absorption Curves.—All the preceding compounds exhibit the characteristic ultra-violet absorption band of the carbonyl group. In the compounds (I) and (II) the absorption curve is symmetrical on a scale of wave-lengths and can be expressed satisfactorily by Lowry and Hudson's equation (Part XXIII, Figs. 1 and 2). The absorption curves (Curve 1, in Figs. 1 and 2) of the open-chain acetates of fructose and fucose, (IV) and (V), however, resemble that of the arabinose acetate, (III), in that they are *steeper on the low-frequency side* (compare *ibid.*, Fig. 3). Hudson (Thesis, Cambridge, 1933, p. 164) has suggested that curves of this kind might be expressed by a general equation of the type

$$\varepsilon = \varepsilon_{\text{max.}}\, e^{\cdot[(\nu_0/\nu)^n(\nu_0-\nu)/\theta]^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ν_0 is the frequency of the maximum and θ is related to the half-width λ' or ν' of the band by $\theta = c\lambda'/1{\cdot}6651\lambda_0^2$ or $\theta = 1{\cdot}6651\nu'$. Attempts were therefore made to apply this equation with $n = 2$, but the theoretical curves still sloped less steeply than the experimental curves on the side of longer wave-lengths.

Circular Dichroism.—The circular dichroism of the fructose and fucose acetates is shown as Curve 2 in Figs. 1 and 2. On the assumption that the dissymmetry factor, $(\varepsilon_l - \varepsilon_r)/\varepsilon$, in a given optically active absorption band, is proportional to the frequency, the circular dichroism for $n = 2$ is given by the equation

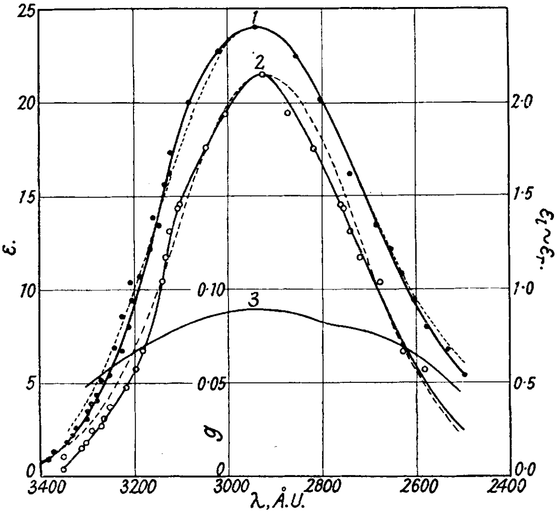
$$(\varepsilon_l - \varepsilon_r) = (\varepsilon_l - \varepsilon_r)_{\text{max.}}\, (\lambda_0/\lambda) e^{\cdot[(\lambda-\lambda_0)/\theta^2]} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

A curve of this kind agrees rather closely with the experimental data for the fructose acetate (Fig. 1), but the approximation is not so good in the case of the fucose acetate (Fig. 2), where the theoretical curve is represented by a broken line.

Complexity of the Carbonyl Absorption Band.—In a homogeneous absorption band, the maxima of absorption and of circular dichroism should occur at approximately the same wave-length, the half-width of the two curves should be the same, and the ratio $(\varepsilon_l \sim \varepsilon_r)/\varepsilon$ should be proportional to the frequency and should therefore increase slightly on passing through the band in the direction of higher frequencies. The complexity of the ketonic absorption band of camphor was disclosed by the fact that the circular dichroism is concentrated on the low-frequency side of the absorption band; and Lowry and Lishmund (this vol., p. 709) have observed an identical displacement of the maximum in carvomenthone. Table III contains the relevant data for the open-chain acetates (I)—(V).

FIG. 2.

Absorption and Circular Dichroism of Tetra-acetyl μ-Fucose.



Curve 1. *Molecular extinction coefficients, ϵ, in chloroform.*
,, 2. *Circular dichroism, $\epsilon_l \sim \epsilon_r$, with curve calculated from Hudson's general equation (n = 2).*
,, 3. *Dissymmetry factor, $(\epsilon_l \sim \epsilon_r)/\epsilon$.*

TABLE III.

Absorption and Circular Dichroism of Open-chain Acetates.

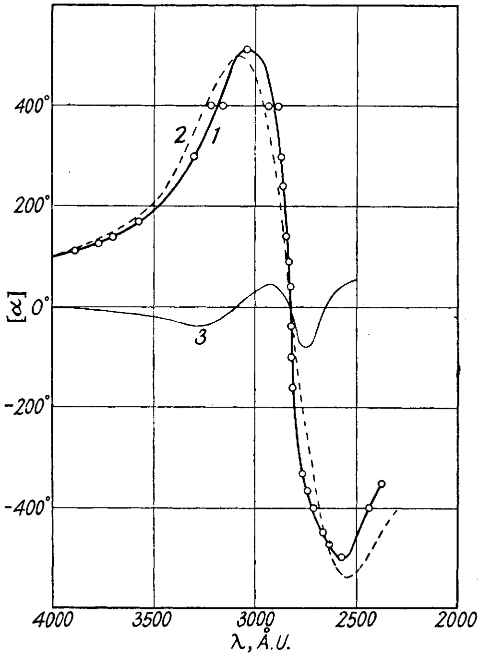
	log ϵ (max.).	Half-width.	$(\epsilon_r - \epsilon_l)$ (max.).	Half-width.
I.	1·505 at 2920 Å.U.	423 Å.U.	1·00 at 2920 Å.U.	420 Å.U.
II.	1·460 ,, 2900 ,,	500 ,,	2·25 ,, 2910 ,,	400 ,,
III.	1·580 ,, 2900 ,,	470 ,,	1·80 ,, 2910 ,,	400 ,,
IV.	1·591 ,, 2830 ,,	472 ,,	1·00 ,, 2800 ,,	392 ,,
V.	1·380 ,, 2935 ,,	520 ,,	2·15 ,, 2924 ,,	446 ,,

In every case the two maxima occur at substantially the same wave-length, so that the displacement of the maximum, observed in the cyclic ketones, is not reproduced in the open-chain aldehydes and ketone now under consideration. In general, however, the half-width of the band of circular dichroism is less than that of the absorption band, with the result that the dissymmetry factor, instead of increasing progressively with decreasing wave-length, passes through a maximum near the middle of the absorption band. This effect is least obvious in penta-acetyl μ-glucose, where the same maximum and half-width were used to calculate the two curves (*loc. cit.*, Fig. 1); conversely, the displacement of the maximum is greatest in the ketone (IV), where it may be as much as 30 Å.U., as compared with 110° in the case of camphor.

The increased width of the absorption band, in comparison with that of the curve of circular dichroism, provides clear evidence of its composite character, and is compatible with the view that the optically active absorption band is accompanied by a wider but weaker and less active band, with a maximum at the same wave-length. This conclusion has already been considered tentatively as an explanation of the fact that absorption bands which are perfectly symmetrical are often pinched at the top and widened at the bottom, in comparison with the calculated curves; but measurements of circular dichroism provide evidence of complexity which is of a more direct and positive character, so that only the origin of the complexity remains open to question. Thus, as an alternative to the preceding suggestion, the falling off of the dissymmetry factor on the side of shorter wave-lengths might be due to overlapping by an inactive " acetate " absorption band of higher frequency; and a falling off on the side of longer wave-lengths has already been attributed in several cases to

FIG. 3.

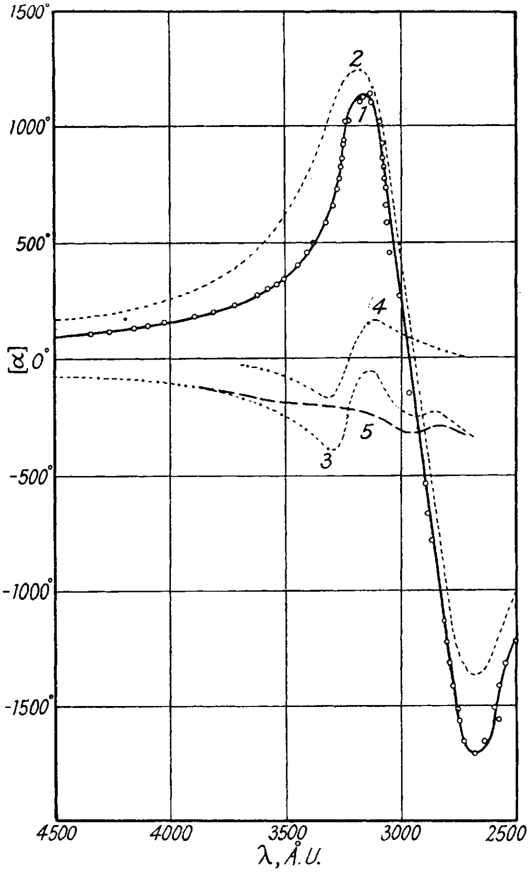
Rotatory Dispersion of Penta-acetyl μ-Fructose.



Curve 1. *Observed rotations.*
,, 2. *Partial rotation of carbonyl group.*
,, 3. *Residual rotation (Curve 1 minus Curve 2).*

FIG. 4.

Rotatory Dispersion of Tetra-acetyl μ-Fucose.



Curve 1. *Observed rotation.*
,, 2. *Partial rotation of carbonyl group.*
,, 3. *Residual rotation (Curve 1 minus Curve 2).*
,, 4. *Subsidiary partial rotation.*
,, 5. *Residual rotation corrected (Curve 3 minus Curve 4).*

the presence of a small optically active band of opposite sign, in close agreement with parallel observations of rotatory dispersion in the region of absorption.

Form of the Dispersion Curves.—The specific rotations of penta-acetyl μ-fructose and of tetra-acetyl μ-fucose are set out in Tables IV and V and are plotted in Figs. 3 and 4.

TABLE IV.

Rotatory Dispersion of Penta-acetyl μ-Fructose at 20°.

(a) : c = 8·68 g./100 c.c.; l = 2 dm.; $[\alpha] = 5{\cdot}764\alpha$.
(b) : c = 1·7616 g./100 c.c.; l = 1 dm.
(c), (d), (e), (f) : c = 1·28, 2·056, 1·028, 1·161 g./100 c.c.; l = 1 cm.
All solutions in chloroform (free from alcohol).

$$[\alpha_1] = \frac{9{\cdot}599}{\lambda^2 - 0{\cdot}06792}; \quad [\alpha_2] = \frac{7{\cdot}4367}{\lambda^2 - 0{\cdot}078664} + \frac{2{\cdot}3036}{\lambda^2}.$$

Visual readings (Soln. a).

λ.	$[\alpha]$.	(O–C) for $[\alpha_1]$.	(O–C) for $[\alpha_2]$.	λ.	$[\alpha]$.	(O–C) for $[\alpha_1]$.	(O–C) for $[\alpha_2]$.	λ.	$[\alpha]$.	(O–C) for $[\alpha_1]$.	(O–C) for $[\alpha_2]$.
Li 6708	25·30°	+0·20°	+0·04°	Ag 5472	41·20°	−0·30°	−0·20°	Zn 4811	58·90°	+0·20°	+0·28°
Cd 6438	27·70	±	±	Hg 5461	41·80	+0·15	+0·18	Cd 4800	59·00	−0·02	±
Zn 6362	27·95	−0·53	−0·53	Cu 5219	46·60	−0·30	−0·25	Zn 4722	61·90	±	±
Li 6104	31·83	+0·36	+0·35	Ag 5209	47·00	−0·15	−0·08	Zn 4680	64·00	+0·50	+0·45
Na 5893	34·30	−0·03	+0·04	Cu 5153	48·50	−0·05	+0·01	Cd 4678	63·10	−0·52	−0·52
Hg 5780	36·00	±	±	Cu 5106	50·00	+0·17	+0·25	Ba 4554	69·35	+0·55	+0·45
Cu 5700	37·20	−0·15	−0·09	Cd 5086	50·35	±	+0·15	Hg 4358	79·30	+0·60	+0·38
Ba 5536	40·35	0·15	+0·18	Ba 4934	54·17	−0·48	−0·40				

Photographic readings (Soln. a).

λ.	$[\alpha]$.	(O–C) for $[\alpha_1]$.	(O–C) for $[\alpha_2]$.	λ.	$[\alpha]$.	(O–C) for $[\alpha_1]$.	(O–C) for $[\alpha_2]$.	λ.	$[\alpha]$.	(O–C) for $[\alpha_1]$.	(O–C) for $[\alpha_2]$.
Fe 4258	84·3	−0·3	−0·9	Fe 3878	119·0	+2·7	+0·1	Fe 3715	142·0	+ 5·1	±
Fe 4185	90·1	+0·6	−0·3	Fe 3821	124·8	+1·9	−1·5	Fe 3594	165·0	+ 8·6	+0·3
Fe 4107	95·8	+0·5	−0·5	Fe 3794	130·5	+4·2	+0·6	Fe 3556	176·5	+12·4	+2·4
Fe 3983	107·3	+1·5	−0·3	Fe 3742	136·2	+3·2	−1·2	Fe 3521	189·0	+18·0	+6·3
Fe 3925	113·2	+2·0	−0·4								

Region of absorption.

Soln.	λ.	α.	$[\alpha]$.	Soln.	λ.	α.	$[\alpha]$.	Soln.	λ.	α.	$[\alpha]$.
b	3417	3·52°	199·7°	d	3205 2900	0·82°	400°	c	2788	−0·04°	− 30°
b	3280	5·28	299·6	c	3018	0·64	500	c	2790	−0·17	−130
c	3230 2858	0·38	300	d	3018	1·03	500	f	2478 2772	−0·41	−350
b	3222	6·82	387·3	e	2850	0·28	270	f	2699 2507	−0·52	−450
c	3175 2858	0·51	400	d	2830	0·15	150	f	2570	−0·58	−500
					2807	0·09	40				

(*a*) In the region of transparency, the rotatory dispersion of penta-acetyl μ-fructose can be expressed by a single term of Drude's equation as far as 4107 Å.U., but a third constant is needed to extend the range to 3594 Å.U., beyond which a fourth constant appears to be required. In the region of absorption, the partial rotation of the carbonyl group was not calculated from the observed circular dichroism, but with the help of an arbitrary factor, selected to give the closest possible fit to the experimental curve. The curve of residual rotations crosses the axis at four points, the largest ripple being due to the fact that Lowry and Hudson's equation does not give equal positive and negative maxima, like the experimental curve.

(*b*) In the region of transparency, the rotatory dispersion of tetra-acetyl μ-fucose was expressed as far as 3547 Å.U. by means of a Drude equation with three constants. In the region of absorption, the partial rotation of the aldehydic group, calculated from the circular dichroism by means of Lowry and Hudson's equation, leaves a substantial *negative* high-frequency rotation when subtracted from the observed total rotation. The curve of residual rotations, however, again shows a substantial ripple in the neighbourhood of the second (negative) maximum. This ripple can be largely reduced by postulating a small optically active band of opposite sign with a maximum at about 3200 Å.U. The existence of such a band can be justified by the steep fall of the foot of the curve of circular dichroism on the side of longer wave-lengths, and is in agreement with similar conclusions already reached in the case of the glucose acetate (*loc. cit.*, Fig. 4).

TABLE V.

Rotatory Dispersion of Tetra-acetyl μ-Fucose at 20°.

(a), (b), (c) : c = 2·108, 2·416, 2·380 g./100 c.c.; l = 2 dm.; $[\alpha_2]$ = about 20α.
(d), (e), (f), (g) : c = 2·380, 1·125, 0·993, 1·039 g./100 c.c.; l = 1 cm.; $[\alpha]$ = 400—1000α.
(a)—(f) in $C_2H_2Cl_4$; (g) in $CHCl_3$.

$$[\alpha] = \frac{11{\cdot}7236}{\lambda^2 - 0{\cdot}09059} - \frac{1{\cdot}8301}{\lambda^2}.$$

Visual readings.

Soln.	λ.	[α].	(O–C).	Soln.	λ.	[α].	(O–C).	Soln.	λ.	[α].	(O–C).
b	Li 6708	28·15°	−0·41°	b	Ag 5472	49·70°	−0·19°	b	Cd 5086	62·70°	±
a	Li 6104	36·71	+0·02	b	Hg 5461	50·50	+0·15	b	Ba 4934	69·15	−0·03°
b	Na 5893	40·20	−0·23	b	Cu 5219	57·80	−0·02	b	Zn 4811	76·20	+0·70
ab	Cu 5782	42·62	±	b	Ag 5209	58·00	−0·25	a	Zn 4722	80·35	+0·05
ab	Hg 5780	42·87	+0·20	b	Cu 5153	60·05	−0·10	b	Cd 4678	83·50	+0·41
b	Ba 5536	48·65	+0·22								

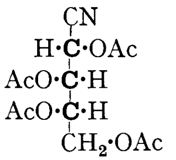
Photographic readings.

Soln.	λ.	[α].	(O–C).	Soln.	λ.	[α].	(O–C).	Soln.	λ.	[α].	(O–C).
c	Fe 4325	111·0	−1·9	c	Fe 4031	150·0	−1·8	c	Fe 3631	270·0	−0·1
c	Fe 4271	120·0	+2·1	c	Fe 3900	180·0	+1·4	c	Fe 3547	320·0	+1·2
c	Fe 4163	130·0	−1·3	c	Fe 3821	200·0	+0·7	c	Fe 3513	340·0	−4·0
c	Fe 4103	140·0	±	c	Fe 3727	230·0	+0·2	c	Fe 3454	400·0	+7·0

Region of absorption.

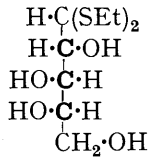
Soln.	[α].	λ.	Soln.	[α].	λ.	Soln.	[α].	λ.
d	450°	3413, 3057	e	1120°	3165, 3125	f	−1080°	2797
d	500	3392, 3057	e	1149	3134	f	−1120	2775
d	580	3330, 3071	e	267	3009	f	−1180	2769
d	660	3298, 3075	e	0	2991	f	−1280	2766
d	730	3280, 3075	e	133	3000	f	−1340	2760
d	770	3275, 3079	e	− 151	2976	f	−1400	2755
d	820	3270, 3083	e	− 285	2970	f	−1500	2750
d	866	3262, 3087	e	− 418	2922	g	+1223	3194, 3150
d	930	3254, 3100	e	− 540	2902	g	−1128	2832, 2510
d	1020	3230, 3100	e	− 668	2898	g	−1225	2820, 2522
d	1100	3180, 3131	e	− 784	2876	g	−1416	2794, 2585
e	819	3265, 3080	f	− 886	2840	g	−1561	2767, 2591
e	916	3257, 3083	f	− 950	2826	g	−1660	2744, 2647
e	1015	3244, 3095	f	−1020	2806	g	−1755	2702

Open-chain Derivatives of Arabinose and Fructose.—The two compounds in which the phenomenon of optical cancellation has been observed are of similar (but opposite) configurations, as regards the three asymmetric carbon atoms which they both contain. Moreover, the first of these atoms is attached in each case to a carbonyl group, and thence to an inactive radical (H or $CH_2{\cdot}O{\cdot}CO{\cdot}CH_3$), the nature of which does not appear to affect the phenomenon. It was therefore of interest to study the rotatory dispersion of other open-chain derivatives containing three asymmetric carbon atoms of similar orientation, in order to ascertain whether the same phenomenon could be detected in them.



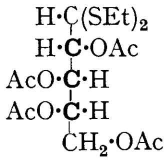
$$\begin{array}{c} CN \\ H{\cdot}\mathbf{C}{\cdot}OAc \\ AcO{\cdot}\mathbf{C}{\cdot}H \\ AcO{\cdot}\mathbf{C}{\cdot}H \\ CH_2{\cdot}OAc \end{array}$$

(VI.) Tetra-acetyl *l*-arabono-nitrile.



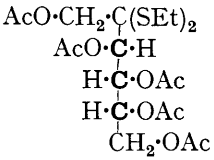
$$\begin{array}{c} H{\cdot}C(SEt)_2 \\ H{\cdot}\mathbf{C}{\cdot}OH \\ HO{\cdot}\mathbf{C}{\cdot}H \\ HO{\cdot}\mathbf{C}{\cdot}H \\ CH_2{\cdot}OH \end{array}$$

(VII.) *l*-Arabinose ethylmercaptal.



$$\begin{array}{c} H{\cdot}C(SEt)_2 \\ H{\cdot}\mathbf{C}{\cdot}OAc \\ AcO{\cdot}\mathbf{C}{\cdot}H \\ AcO{\cdot}\mathbf{C}{\cdot}H \\ CH_2{\cdot}OAc \end{array}$$

(VIII.) Tetra-acetyl *μ*-*l*-arabinose ethylmercaptal.



$$\begin{array}{c} AcO{\cdot}CH_2{\cdot}C(SEt)_2 \\ AcO{\cdot}\mathbf{C}{\cdot}H \\ H{\cdot}\mathbf{C}{\cdot}OAc \\ H{\cdot}\mathbf{C}{\cdot}OAc \\ CH_2{\cdot}OAc \end{array}$$

(IX.) Penta-acetyl *μ*-*d*-fructose ethylmercaptal.

Unlike the five preceding compounds, these four derivatives, (VI)—(IX), exhibit only a general absorption in the accessible ultra-violet region. The absorption bands of the terminal radicals, therefore, lie in a region in which the Cotton effect cannot at present be observed. For this reason, the presence or absence of optical cancellation could not be established by the same direct method as in the two preceding cases, *viz.*, by observations of rotatory dispersion in the region covered by an optically active absorption band.

The rotatory dispersions in the region of transparency are set out in Table VI. These

TABLE VI.

Rotatory Dispersion of Open-chain Derivatives of Arabinose and Fructose at 20°.

(VI) (a) c = 3·1635 g./100 c.c.; l = 6 dm.; (b) l = 1 dm.
(VII) (a) c = 4·599 g./100 c.c.; l = 6 dm.; (b) c = 3·369 g./100 c.c.; l = 2 dm.
(VIII) (a) c = 4·1563 g./100 c.c.; l = 6 dm.; (b) c = 3·6319 g./100 c.c.; l = 1 dm.
(IX) (a) c = 3·9341 g./100 c.c.; l = 6 dm.; (b) c = 3·0593 g./100 c.c.; l = 1 dm.
(VI), (VIII), (IX) in ethyl acetate; (VII) in formamide.

Visual readings.

		Soln. VI (a). [α] = 5·268α.		Soln. VII (a). [α] = 3·623α.		Soln. VIII (a). [α] = 4·010α.		Soln. IX (a). [α] = 4·237α.	
λ.		[α].	(O–C).	[α].	(O–C).	[α].	(O–C).	[α].	(O–C).
Cd	6438	3·972°	−0·02°	− 4·71°	+0·02°	−16·48°	−0·13°	12·71°	−0·13°
Na	5893	4·952	+0·12	− 5·66	+0·23	−20·21	−0·11	15·67	±
Hg	5780	5·110	+0·08	− 6·17	+0·02	−21·26	−0·21	16·56	+0·17
Ag	5468	—	—	− 7·18	−0·03	—	—	—	—
Hg	5461	5·690	±	− 6·96	+0·21	−24·26	+0·06	18·80	+0·10
Ag	5209	6·006	−0·29	− 8·12	+0·04	—	—	—	—
Cd	5086	6·480	−0·16	− 8·66	+0·04	−28·71	+0·11	21·85	−0·25
Cd	4800	7·271	−0·29	−10·27	+0·08	−33·69	−0·19	25·07	−0·35
Cd	4678	7·692	−0·32	—	—	−35·49	+0·34	26·90	−0·19
Hg	4358	9·588	+0·18	−13·49	+0·35	−43·27	+0·23	32·35	−0·05

Photographic readings.

Soln.	λ.	[α].	(O–C).	Soln.	λ.	[α].	(O–C).	Soln.	λ.	[α].	(O–C).
VI (a)	4230	10·05°	−0·02°	VIII (a)	4360	− 43·30°	+0·10°	VIII (b)	2901	−202·3°	− 3·0°
,,	4096	10·85	±	,,	4176	− 49·32	−0·20	,,	2872	−217·5	− 6·2
,,	4000	11·51	+0·01	,,	4029	− 54·13	+0·52	,,	2868	−217·5	− 4·1
,,	3821	12·95	+0·14	,,	3886	− 60·55	+0·55	,,	2843	−228·5	− 3·9
,,	3631	14·50	±	,,	3720	− 69·37	+0·8	IX (a)	4335	32·32	− 0·53
VI (b)	3576	15·16	+0·15	VIII (b)	4434	− 41·3	+0·2	,,	4213	35·70	+ 0·30
,,	3350	17·72	−0·03	,,	4045	− 53·7	+0·3	,,	4137	37·83	+ 0·69
,,	3203	19·95	+0·05	,,	3764	− 68·8	−1·2	,,	3990	40·78	− 0·21
VII (b)	4680	−10·98	+0·11	,,	3694	− 72·9	−0·3	,,	3930	43·20	+ 0·45
VII (a)	4396	−13·57	+0·09	,,	3581	− 79·9	+0·1	,,	3780	47·43	− 0·10
,,	4260	−15·00	−0·09	,,	3513	− 86·7	−1·1	,,	3714	50·11	±
,,	4144	−16·46	−0·05	,,	3426	− 93·6	+0·1	,,	3605	54·85	+ 0·23
,,	4031	−17·91	+0·19	,,	3339	−103·2	+0·4	,,	3530	58·03	− 0·27
,,	3939	−19·37	+0·35	,,	3271	−111·5	+0·9	IX (b)	3650	50·0	− 2·7
VII (b)	3792	−22·85	+0·07	,,	3108	−140·4	−0·1	,,	3346	68·7	− 0·2
,,	3541	−28·77	+2·27	,,	3047	−154·2	±	,,	3040	101·2	+ 5·2
				,,	2992	−169·3	−0·5	,,	2912	134·0	+20·8
				,,	2929	−188·6	+0·3	,,	2836	161·8	+35·3

are approximately simple, since the specific rotations could be expressed in each case by a single term of Drude's equation, as follows:

	(VI.)	(VII.)	(VIII.)	(IX.)
[α] =	$\frac{+\ 1{\cdot}5577}{\lambda^2 - 0{\cdot}024415}$	$\frac{-\ 1{\cdot}6123}{\lambda^2 - 0{\cdot}073461}$	$\frac{-\ 5{\cdot}8874}{\lambda^2 - 0{\cdot}054661}$	$\frac{+\ 4{\cdot}7717}{\lambda^2 - 0{\cdot}042714}$
λ_0, Å.U. =	1563	2710	2338	2066

The value λ_0 = 1563 Å.U. for the nitrile is not far removed from the value λ_0 = 1460 Å.U. for sucrose (Lowry and Richards, J., 1924, **125**, 2523; Harris, Hirst, and Wood, J., 1932, 2115). This is in harmony with the fact that the absorption bands of the cyanides, as deduced from measurements of refractive dispersion (Lowry and Henderson, *Proc. Roy. Soc.*, 1932, *A*, **136**, 471), appear to lie in the same region of the spectrum as those of the hydroxyl group. It was therefore impossible to break up the total rotation in such a way as to assign a partial rotation to the cyanide radical. On the other hand, the dispersion constants of the three mercaptals are much larger than those of the simple sugars. They thus afford clear evidence of the existence of new partial rotations, which are not present in the sugars themselves; but the inequality of these coefficients makes it impossible to assign the whole of the rotations to the induced activity of the mercaptal group, since this would be expected to have the same characteristic frequency throughout. Hence, we conclude that the rotatory dispersions of some, at least, of these four derivatives are only pseudo-simple, and that their observed total rotations must consequently include partial rotations due to the asymmetric carbon atoms, as well as to the mercaptal radicals. There is thus quite clear evidence that the optical cancellation observed in the aldehydic acetates of arabinose and fructose does not persist as a general phenomenon in these derivatives of the two sugars, and so it appears probable that the carbonyl group is essential to the balance of opposite partial rotations which leads to this effect in the two aldehydic acetates cited above.

The substances were prepared at the Ohio State University. When used in Cambridge their m. p.'s were found to agree closely with the published values.

The methods used for measurements of absorption, circular dichroism, and rotatory dispersion have already been described, but a novel feature is found in the use of four *barium* lines, *viz.*, λλ 6496·91, 5535·53, 4934·10, and 4554·037, to fill up gaps in the series of lines used previously in spectro-polarimetry.

SUMMARY.

The phenomenon of optical cancellation, already observed in tetra-acetyl μ-arabinose, occurs also in penta-acetyl μ-fructose, where the three asymmetric carbon atoms have the same relative configuration, but are of opposite signs. Other open-chain derivatives of arabinose and fructose, in which there is no carbonyl group attached to the first asymmetric carbon atom, do not show this effect.

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